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WETTABLE POWDER versus TANK-MIX DITHIOCARBAMATES on POTATOES and TOMATOES in OHIO

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J. D. WILSON

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OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER, OHIO

CONTENTS

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INTRODUCTION

The dithiocarbamates have now been used as fungicides in Ohio, experimentally or otherwise, for more than 15 years (4). Fermate (ferbam), or ferric dimethyl dithiocarbamate, was the first of these to be used on tomatoes and potatoes, to which it was applied both as spray and dust mixtures prepared from a wettable powder formulation (1, 2).

Dithane and Parzate have now been tested experimentally for several years both as wettable powders (zineb) and as "tank-mix" formulations of solubilized zinc sulfate plus liquid disodium ethylene bis dithiocarbamate (nabam). There has always been some question as to which type of formulation is capable of giving the best control of such diseases as the early and late blights of potato and tomato (10, 12). During the same period, as good or better results were being obtained with a slurry form of zinc dimethyl dithiocarbamate than with the corresponding wettable powders known as Zerlate and Methasan (ziram) (16, 17, 18).

The wettable powder formulations of such fungicides as ferbam, ziram, and zineb are prepared by the manufacturer for use in spray and dust applications. The active ingredients of these powder formulations, which are comparatively insoluble and non-wettable, are made wettable by adding wetting and/or conditioning agents. The finished product must be sufficiently wettable that it may be completely and thoroughly mixed with water in the form of a suspension in the sprayer tank, but still not so easily wettable that it will quickly wash off the foliage during the first rain that occurs after it is applied. The wettable powders must also be very finely ground if they are to give the maximum degree of plant coverage and disease control.

In contrast to the wettable powders, the individual particles of the fungicidal ingredient that are formed in the sprayer tank when a material such as zineb is prepared by mixing zinc sulfate and nabam (see Appendix), are comparatively smaller and are already wetted (in

the absence of a wetting agent). Such particles can be easily kept in suspension with a minimum of agitation while the spray formulation is being applied to the plant foliage.

It is with comparisons, during a period of three years, between these wettable powders, as they are prepared by the manufacturer, and their corresponding tank-mix formulations, as they are prepared in the field just before they are to be applied, that the experiments discussed in this paper are primarily concerned.

PRELIMINARY WORK

A forerunner of Dithane (nabam and/or zineb), then known under the code number of HE-175, was first used as a spray mixture in a series of potato treatments in 1943 (4). In 1944, Dithane was again used on potatoes as Dithane D-14 plus $ZnSO_4$ in a tank-mix formulation, and as a wettable powder (4). Zerlate and Methasan (zinc dimethyl dithiocarbamate), which now have the common name of ziram, were used in wettable powder spray formulations in 1944 (3). Ferbam, as Fermate, was tested further on both tomatoes and potatoes in 1944 (4, 5), but ziram, as either Zerlate or Methasan, was largely substituted for ferbam on these crops after that date (6). Zineb, as Dithane Z-78, a wettable powder formulation of zinc ethylene bis dithiocarbamate, was included in the fungicide trials on potatoes and tomatoes in 1945 (7). A wettable powder formulation of nickel ethylene bis dithiocarbamate, which has never come into use, was tested in 1945 and 1946 (7, 13). This was followed in 1946 by a sample of manganese ethylene bis dithiocarbamate (no common name as yet) prepared as a wettable powder that has since come to be known under the trade name of Manzate (8). It was used on potatoes and tomatoes at that time. Parzate was included in the experimental trials in the form of both nabam and zineb in 1947 (9).

Two modified carbamate formulations under the names of Zac (zinc dimethyl dithiocarbamate-cyclohexylamine) and Vancide 51 (a 50-50 mixture of zinc dimethyl dithiocarbamate and 2-mercaptobenzothiazole) also appeared in the list of experimental materials about 1947 or 1948 (15, 16). Methasan (ziram) was first prepared as a slurry and used in 1947 (9), and Zac was similarly formulated in 1948 (15, 16). Various 2-, 3-, and 4-metal dithiocarbamates have also been tested in recent years in a search for possible synergistic and/or nutritional effects (15, 16, 17, 18), but none have shown any worthwhile improvement over the various single metal formulations.

Dithane D-14 and Parzate were the only liquid dithiocarbamates that were included in the experimental program on vegetables in Ohio up to and including 1949. In 1950 Vancide 51 was used on tomatoes and potatoes (14, 17). In 1951 and 1952, tank-mix formulations of several dithiocarbamates were compared with the corresponding wettable powders, as they were made by the manufacturer, for the control of the early and late blights of potato and tomato (17, 18). See Appendix. Dithane and Parzate (zineb) were prepared in the usual way by adding zinc sulfate to nabam. The precipitate corresponding to Manzate was obtained by adding manganese sulfate to nabam. Tank mixtures similar to Zerlate and Methasan (zirams) were made by adding $ZnSO_4$ to sodium dimethyl dithiocarbamate. This same liquid was combined with ferric sulfate to duplicate Fermate (ferbam). A formulation of sodium dimethyl dithiocarbamate and cyclohexylamine was mixed with $ZnSO_4$ to duplicate Zac. Vancide 51 plus $ZnSO_4$ gave a precipitate similar to Vancide ZW.

Late blight, caused by **Phytophthora infestans** DeB., was severe at some points in Ohio, including Wooster, in 1950, but it was scarce in 1951 and virtually absent in 1952. Early blight, caused by **Alternaria solani** J. & G., was of medium sevêrity over most of Ohio in 1950 and 1951, but was less common in 1952. It caused an average degree of defoliation of potatoes at Marietta and Wooster in 1951 and 1952, but was severe on muck-grown potatoes at Willard (Celeryville) during both of these seasons. Early blight was of medium severity on tomatoes at Wooster in 1951 and somewhat less destructive in 1952. Late blight did not appear in the experimental tomato plots at Wooster in 1951 or 1952, but caused a great deal of defoliation and fruit rot in 1950 (14). Thus, the data presented here for potatoes and tomatoes for the summers of 1951 and 1952 deal almost entirely with the control of early blight, and only data collected in 1950 and earlier offer any comparisons relative to the control of late blight.

The "dimethyl" dithiocarbamates (Fermate, Zerlate, Methasan, Zac, and Vancide) are known from previous experiments (13, 14) to be comparatively ineffectual against late blight, but some of them at least may be expected to give comparatively good control of early blight and tomato anthracnose caused by **Colletotrichum phomoides** (Sacc.) Chester, (11, 12, 13, 15, 16, 17, 18). The "ethylene bis" dithiocarbamates (Dithane, Parzate, and Manzate), on the other hand, are quite effective against both early and late blights (12, 13, 14).

RESULTS AND DISCUSSION

Following the early use of Fermate on tomatoes (1) and potatoes (2), Zerlate and Methasan were used experimentally, as wettable powders, on both crops during the period from 1944 to 1950. In 1947 (9), Methasan was first applied as a slurry in which the original preparation was not dried following its manufacture. It soon became apparent that the slurry would give better control of early blight than did the wettable powder. This is indicated in Table 1 in which data relative to the average performance of the two formulations are given for 11 different experiments. These were conducted over a period of 4 years on both potatoes and tomatoes. Late blight appeared in some of the experiments, as is indicated in the fourth column of the data relative to tomatoes. These data show that the slurry formulation gave an average yield increase over the wettable powder of one ton per acre. This increase was largely the result of a 3.9 percent reduction in the fruits that had to be discarded as culls. Some of these were classified as culls because of anthracnose fruit rot which occurred in all experiments, and a still larger portion were discarded because of late blight lesions in the five experiments where that disease occurred. Both diseases were better controlled by Methasan as a slurry than by either Zerlate or Methasan as wettable powders.

TABLE 1. Comparative effectiveness of zinc dimethyl dithiocarbamate as a wettable powder (Zerlate and/or Methasan) and as a slurry (Methasan) in the control of early and late blights on potato and tomato during a period of 4 years. Data are averages of 11 experiments on each crop.

Formulation	Net yield Tons/Acre	Percent Culls	Percent Anthracnose	Percent Late blight on fruits in 5 expts.	Percent Defoliation
Tomato					
Wettable powder	17.1	17.1	2.4	19.6	45
Slurry	18.1	13.2	1.7	10.4	32
No treatment	14.2	26.1	5.7	38.7	70
Potato					
	Yield in Bu./Acre	**Percent Defoliation**			
Wettable powder	493	38			
Slurry	505	32			
No treatment	409	80			

Comparisons between the two types of formulation were also made on potatoes. The data relative to these experiments are given in the second portion of Table 1. The results with respect to yield and defoliation were similar to those obtained on tomatoes. The average yield from 11 experiments in which comparisons were made was 12 bushels per acre larger with Methasan used as a slurry than when the sprays were prepared with the wettable powder of either Methasan or Zerlate. This yield excess in favor of the slurry was chiefly due to the better control that it gave of both early and late blights on the potato foliage.

Dithane D-14 plus $ZnSO_4$, and its wettable powder counterpart in Dithane Z-78, have been compared on tomatoes and potatoes for several years in Ohio. Some of the data collected on tomatoes from 1948 to 1951, inclusive, are given in Table 2. These data are averages of seven different experiments. The wettable powder (Z-78) gave a slightly higher yield, fewer culls and somewhat better control of defoliation than did the tank mixture of Dithane D-14 and $ZnSO_4$. The latter gave slightly better control of the fruit rots caused by anthracnose and late blight than did Dithane Z-78. As a result of these counterbalances, the two formulations gave results as closely comparable as one might ever expect to find in comparisons of this kind.

Late blight of tomato was very prevalent over much of Ohio in 1950. It was especially severe in several of the experimental plots at Wooster, and as a result it was possible to obtain a very good comparison of the ability of various fungicides to control the disease (14). Some of the data relative to differently formulated dithiocarbamates are given in Table 3, for two different experiments.

TABLE 2. Relative effectiveness of Dithane D-14 + $ZnSO_4$, and Z-78, in the control of tomato diseases. Data are averages of 7 different experiments covering 4 different years. Early blight and anthracnose were present in all seven, and late blight in four of the experiments.

Treatments	Net yield Tons/Acre	Percent Culls	Percent Anthracnose	Percent Defoliation	Percent of fruits with late blight in 4 expts.
Dithane D-14 + $ZnSO_4$	19.7	10.6	2.23	31	5.1
Dithane Z-78	20.0	10.4	2.55	30	5.8
No treatment	13.2	31.2	5.23	70	48.2

TABLE 3. Comparative control of tomato diseases (early and late blights and anthracnose) by variously formulated dithiocarbamates at Wooster in 1950. Late blight was severe, early blight medium, and anthracnose very light.

	Net yield in Tons/Acre	Percent Culls	Percent of fruits with anthrac-nose	Percent of fruits with late blight	Percent Defoli-ation
Experiment I					
No treatment	5.9	73.5	2.5	87.5	84
Methasan wettable	14.4	47.7	0.6	45.4	52
Methasan slurry	19.4	25.6	0.0	15.9	32
Zac wettable	8.7	62.7	0.7	69.5	74
Zac slurry	7.8	60.3	0.1	56.5	57
Parzate (Dry)	22.0	18.6	0.3	11.7	29
Dithane D-14 + $ZnSO_4$	21.8	17.0	0.3	9.0	34
Experiment II					
No treatment	10.4	33.1	3.0	35.4	71
Parzate (Dry)	16.0	9.3	1.2	6.0	35
Parzate L + $ZnSO_4$	17.0	7.4	0.6	2.9	37
Zerlate	13.5	27.8	0.2	29.2	54
Methasan slurry	15.8	12.1	0.1	9.0	30

Experiment I. Late blight became so destructive in this experiment that the untreated check plots had lost 84 percent of their foliage and 87.5 percent of their fruit by the end of the harvest period. The difference in control effectiveness between Methasan as a wettable powder and as a slurry is well demonstrated in this experiment. The percentage in number of fruits showing late blight lesions was reduced from 87.5 only to 54.4 percent by the powder, whereas this was further decreased to 15.9 percent by the slurry. Anthracnose was reduced to 0.6 percent by the wettable powder and virtually eliminated by the slurry. As a result of this difference in control efficiency the reduction in the weight of culls from 73.5 percent in the untreated check to 47.7 percent by the powder was still further decreased to 25.6 percent by the slurry. This resulted in a five tons per acre increase in yield for the slurry over the wettable powder. Defoliation was reduced from 84 percent in the untreated check to 32 percent by the slurry form of Methasan, which wasn't very different from the average values for the Parzate and Dithane plots. Zac slurry was somewhat better than the

wettable powder in disease control but the yield was no greater. The over-all performance of dry Parzate and tank-mix Dithane was very similar in this experiment.

Experiment II. Late blight was not as serious in this test as in the first experiment of Table 3, but early blight was somewhat more prevalent. There was not very much difference between the results obtained with the dry and liquid Parzate formulations in this trial, but the tank mixture was slightly the better in all categories except the control of defoliation. Methasan slurry, however, again gave much better control of late blight than did the wettable powder, which in this instance was Zerlate.

In a third experiment where late blight was comparatively severe (60 percent of the fruits affected and a defoliation percentage of 79 in the untreated check), the difference between Methasan slurry and Zerlate, and also between tank-mix Dithane and dry Parzate, was insignificant.

During the last several years the fungicide comparisons on potatoes in Ohio have been made at three and sometimes four locations on as many different soil types (16, 17, 18, 19), in an effort to more accurately classify the different materials being used on the basis of their disease-control effectiveness. The data of Table 4 represent a comparison between tank-mix and wettable-powder formulations of Dithane. The average yield and defoliation values are given for a sandy loam at

TABLE 4. Comparative effectiveness of Dithane D-14 + $ZnSO_4$, and Z-78, in the control of early and late blights of potato during a 5-year period at three different locations. Data are averages of 15 comparisons, with late blight present in five of them.

Year	Yield in Bu./Acre			Percent Defoliation		
	Dithane D-14 + $ZnSO_4$	Dithane Z-78	No treatment	Dithane D-14 + $ZnSO_4$	Dithane Z-78	No treatment
1948	601	590	403	32	29	79
1949	553	533	427	32	34	85
1950	511	511	411	24	29	79
1951	515	505	314	29	32	86
1952	376	406	304	31	31	62
Averages	511	509	372	30	31	78

Marietta, silt loams at Wooster and Apple Creek, and a muck soil at either McGuffey or Willard. A total of 15 different experiments contributed to these data, with late blight being present in five of them and early blight in all. The average yield and defoliation values for all 15 trials was very similar for the spray formulations prepared from the wettable powder and by adding zinc sulfate to Dithane D-14. This further confirms the statement previously made with reference to the tomato data of Table 3, that there is comparatively little difference between these two formulations of zinc ethylene bis dithiocarbamate in their effectiveness for the control of the early and late blights of tomato and potato.

The excellent results obtained with the slurry form of Methasan, and the difficulty experienced in packaging the manufactured preparation, made it seem desirable to try a tank-mix formulation of ziram that could be prepared in the same way as a spray-tank mixture of zineb. This was done in 1951 when several of the "dithiocarbamate" formulations that could be easily prepared were compared on potato and tomato (12, 18). The data relative to potatoes are given in Table 5. Early blight was present in varying degrees at each of the four locations. Late blight was virtually absent, with a very slight infection at Marietta. Zerlate and Dithane Z-78 were used in a 2-100 formula; SDDC, SDDC-A, and Vancide 51 were each used with $ZnSO_4$ in a 4-1-100 tank mixture, as was Dithane D-14 with $ZnSO_4$ and with $MnSO_4$. The tank-mix formuations of the "dimethyl" group were prepared by adding a comparatively dilute solution of $ZnSO_4$ in water to either sodium dimethyl dithiocarbamate (SDDC), to a complex of SDDC and cyclohexylamine (SDDC-A), or a mixture of the sodium salts of dimethyl dithiocarbamic acid and 2-mercaptobenzothiazole (Vancide 51).

The average yields obtained with Zerlate as a wettable powder and the tank-mixtures of the other three members of the "dimethyl" group were very similar, although at every location the plots treated with each of the tank-mix formulations somewhat exceeded the wettable-powder yield. Zerlate was more clearly inferior to the tank-mix formulations in the control of defoliation, most of which was caused by early blight. The average defoliation percentages were the same for all three of the tank-mix formulations, and this value was 10 percentage points below that for Zerlate.

Zinc ethylene bis dithiocarbamate was used as Dithane Z-78 (zineb) and the tank-mix formulation of nabam plus $ZnSO_4$ and man-

TABLE 5. Comparative effectiveness of differently formulated dithiocarbamates in the control of early blight of potato at four locations in 1951

Location	"Di-methyl" Group				"Ethylene bis" Group				No treatment	L.S.D. values at odds of 19:1
	Zerlate	SDDC + * $ZnSO_4$	SDDC-A + * $ZnSO_4$	Van. 51 + * $ZnSO_4$	Dithane Z-78	SEBD + * $ZnSO_4$	Manzate	SEBD + $MnSO_4$		
Yields (Bu./Acre)										
Marietta	391	394	395	407	391	396	389	389	314	29
Apple Creek	536	542	563	542	533	560	544	536	436	34
Wooster	566	570	590	568	573	596	572	601	424	32
Willard	527	531	532	564	552	554	538	550	475	53
Averages	505	509	520	520	510	526	511	519	412	
Defoliation (%)										
Marietta	50	35	34	37	35	30	43	42	86	
Apple Creek	26	22	25	22	26	23	25	30	81	
Wooster	49	34	29	27	27	27	31	52	100	
Willard	35	30	30	30	33	30	30	28	80	
Averages	40	30	30	30	30	27	32	38	87	

*SDDC=sodium dimethyl dithiocarbamate, and SDDC-A indicates the addition of cyclohexylamines.
Vancide 51 is a 50-50 mixture of SDDC and sodium mercaptobenzothiazole.
SEBD=disodium ethylene bis dithiocarbamate (nabam).

ganese ethylene bis dithiocarbamate as a wettable powder (Manzate) was compared with the tank-mix formulation prepared by adding $MnSO_4$ solubilized in water to Dithane D-14 (nabam). The precipitate obtained when $MnSO_4$ is added to nabam is subject to considerable variation in its physical characteristics and for this reason, special techniques must be employed. Even then, the results are variable in field operations and for this reason the tank-mix method of formulating manganese ethylene bis dithiocarbamate is not at present recommended. In spite of this inherent variation in the end product, the yields obtained with tank-mix formulation compared very favorably with those that resulted from the use of Manzate. Defoliation, however, was better controlled by Manzate than with the tank-mix preparations. Dithane Z-78 proved in this experiment to be slightly inferior to the tank-mix formulation of Dithane D-14 plus $ZnSO_4$ in most instances, both with respect to yield and the control of defoliation. Many of the variations or differences in yield and disease control that appear in Table 5 are well within the limits of experimental error.

What happened when several of the same fungicides as those listed in Table 5 were used on tomatoes in two different experiments at Wooster in 1951 is shown in Table 6. Early blight was of medium severity and late blight was absent. Anthracnose was comparatively scarce and did not exceed one percent of the total yield in any plot. Methasan slurry and the tank-mix formulation (SDDC + $ZnSO_4$) both gave better control of the defoliation caused by early blight than did wettable Methasan. The corresponding yields were also larger, chiefly because of the better foliage protection, since there was little difference between the three treatments in the percentage of culls. These statements relative to the different Methasan formulations are also applicable to those of Zac. The tank-mix formulation gave the best control of defolation and anthracnose, the fewest culls and the largest yield. Tank-mix Vancide was also somewhat better in most categories than the wettable powder (Vancide 632).

In the "ethylene bis" group there was little to choose between the tank-mix formulation and the wettable powder for either the zinc or the manganese salts. Manzate gave somewhat better control of early blight and anthracnose than its corresponding tank mixture, but the difference in disease control was not great enough to affect the yield.

Potatoes were sprayed with 24 different fungicide-insecticide formulations at three different locations in Ohio in 1952 (18). The data relative to these "dithiocarbamate" formulations are given in Table 7. Comparatively light infections of early blight occurred at

TABLE 6. Comparative effectiveness of differently formulated dithiocarbamates in the control of early blight and anthracnose of tomatoes at Wooster in 1951. Data are averages of two experiments.

Treatments	Yield in Tons/Acre	Percent Culls	Percent Anthracnose	Percent Defoliation
"Di-methyl" group				
Methasan W	17.9	3.61	0.21	41
Methasan S	19.8	3.71	0.27	33
SDDC + $ZnSO_4$	20.4	2.94	0.09	31
Zac Wettable	17.0	3.36	0.45	52
Zac Slurry	18.8	3.67	0.35	41
SDDC-A + $ZnSO_4$	19.2	3.08	0.23	36
Vancide 632	16.7	3.16	0.17	43
Van. 51 + $ZnSO_4$	18.9	2.90	0.25	36
"Ethylene bis" group				
Dithane Z-78	18.6	3.69	0.44	29
SEBD + $ZnSO_4$	16.9	3.80	0.61	26
Manzate	18.0	3.60	0.66	34
SEBD + $MnSO_4$	19.0	3.99	0.97	47
No treatment	15.8	4.55	0.60	65
L.S.D. at odds of 19:1	2.0			
Averages				
Di-methyl group				
Dry powder	17.5	3.38	0.28	45
Tank-mix	19.5	2.97	0.19	34
Ethylene bis group				
Dry powder	18.3	3.65	0.55	32
Tank-mix	18.0	3.90	0.79	37

Wooster and Marietta, but the disease was severe at Willard. Wettable powder and tank-mix formulations of Parzate, Manzate, Zerlate, and Vancide were compared at all three locations, and in addition, Zac and Fermate were used in a fourth experiment at Wooster.

There was little difference in performance between the two formulations of Parzate but the wettable powder was slightly the better in these four experiments. Manzate, the wettable powder form of manganese ethylene bis dithiocarbamate, gave somewhat better control of the defoliation due to early blight and also a higher yield than did the tank-mix formulation.

When the dimethyls Zerlate and Vancide, at all three locations, together with Zac and Fermate, are considered, it is evident that the tank-mix preparations were considerably more effective than the wettable powders in controlling defoliation, and at the same time in increasing the yield of potatoes.

Six different fungicides were applied to tomatoes, both in the form of wettable powders and tank-mix formlations in 1952 (18). The data relative to this experiment are given in Table 8. Early blight was of only medium severity and it appeared comparatively late in the season. Late blight was absent and anthracnose was of only minor consequence. Here again, as with potatoes (Table 7), the dimethyl dithiocarbamates in the form of Zerlate, Zac, Fermate, and Vancide 51, gave considerably

TABLE 7. Comparative results obtained in the control of early blight on potatoes at three locations in Ohio in 1952. Infection light in all except Willard experiment where it was severe.

	Average of experiments at 3 locations		Experiment IV located at Wooster	
	Yield Bu./Acre	Percent Defoliation	Yield Bu./Acre	Percent Defoliation
Parzate	406	31	244	35
SEBD + $ZnSO_4$	376	31	244	38
Manzate	390	33	266	39
SEBD + $MnSO_4$	380	40	245	43
Zerlate	385	34	229	44
SDDC + $ZnSO_4$	404	27	251	27
Vancide ZW	370	40	231	39
Van. 51 + $ZnSO_4$	374	33	266	32
Zac wettable			243	34
SDDC-A + $ZnSO_4$			263	29
Fermate			227	37
SDDC + $FeSO_4$			235	40
No treatment	304	62	168	58
L.S.D. values at odds of 19:1	*		26	
"Dimethyls" only				
Wettable powders	378	37	233	39
Tank-mixtures	389	30	254	32

*L.S.D. values of 15, 23, and 25 bushels per acre at Marietta, Wooster, and Willard, respectively.

better control of early blight when applied as the tank-mix formulations than when used as the corresponding wettable powders. This was less true of Fermate than of the other materials used in the data of both Tables 8 and 7, which indicates that tank-mix Fermate is the least likely of this group of dimethyl dithiocarbamates to be superior to its corresponding wettable powder. The percentage of the total fruit yield that is still green at the end of the harvest season is an excellent indicator of general vine condition at that time. These data, as given in the last column of Table 8, indicate that the tank-mix formulations of the dimethyl dithiocarbamates were all more effective in maintaining the tomato vines in good condition than were the wettable powders of the same fungicides.

This was not true of the ethylene bis dithiocarbamates as represented by Dithane and Manzate. In both instances, the plants sprayed

TABLE 8. Comparative effectiveness of six different dithiocarbamates in controlling a light infection of early blight on tomatoes at Wooster in 1952 when used as wettable powders and as tank-mix preparations.

Treatments	Total yield Tons/Acre	Percent Culls	Percent Defoliation	Percent of yield harvested green
Zerlate	18.2	8.0	72	15.7
SDDC + $ZnSO_4$	20.9	7.3	57	18.8
Zac wettable	15.2	8.9	87	15.0
SDDC-A + $ZnSO_4$	19.1	8.7	51	22.9
Fermate	15.6	8.8	82	14.9
SDDC + $FeSO_4$	16.7	7.5	82	22.0
Vancide ZW	17.7	7.2	72	16.3
Van. 51 + $ZnSO_4$	19.0	7.8	62	20.0
Dithane Z-78	20.1	6.1	44	25.8
SEBD + $ZnSO_4$	20.5	6.5	45	23.4
Manzate	20.0	7.2	39	28.3
SEBD + $MnSO_4$	18.9	7.3	59	24.7
No treatment	14.4	8 6	91	10.5
L.S.D. values at odds of 19:1	2.0			
"Dimethyls only				
Dry powders	16.7	8.2	78	15.5
Tank-mixtures	19.0	7.8	63	20.9

with the wettable powder formulations had more green fruits and showed less defoliation at the end of the season than did those treated with the tank-mix preparations.

A severe attack of early blight on staked tomatoes grown at Marietta was best controlled in 1952 by Parzate used as a wettable powder. This was followed in decreasing order of control by Manzate (wettable powder), nabam plus $ZnSO_4$, SDDC plus $ZnSO_4$, Zerlate (wettable powder), and nabam plus $MnSO_4$. There was little difference between Zerlate and the tank-mix manganese material. Tank-mix ziram was considerably better than Zerlate and only slightly poorer than tank-mix zineb in the control of early blight on these tomatoes. In 1951 tank-mix ziram (SDDC plus $ZnSO_4$) was also somewhat less effective than Manzate and dry Parzate.

In an evaluation of these data, re-assembled on the basis of the fungicidal formulations that were used, Methasan slurry was found to be much more effective in the control of early and late blights on tomatoes than was the wettable powder formulation (ziram). The slurry was also somewhat more effective against anthracnose fruit rot than was ziram. This is a disease against which the wettable powders of Zerlate and Methasan are considered to be among the best fungicides available. In averages of the data from 13 experiments on tomatoes in which a comparison was made between Methasan slurry and either Methasan or Zerlate as a wettable powder, the slurry-treated plots showed 14 percent less defoliation of the kind due to either early blight alone or to a combination of it and late blight, only half as much late blight rot on the fruit, less anthracnose fruit rot, and only two-thirds as many culls as those treated with the wettable powders. The yield difference was 1.4 tons per acre of tomatoes in favor of the slurry-treated plots. On potatoes, the slurry form of Methasan gave an average yield increase over Methasan or Zerlate powders of 12 bushels per acre, and it gave considerably better control of defoliation (32 percent defoliation as compared to 38 percent, respectively.

In an average of four experiments on potatoes in Ohio in 1951, when early blight was of medium severity and late blight absent, a tank-mix formulation of SDDC plus $ZnSO_4$ gave a somewhat better yield than Zerlate, and considerably better control of defoliation. In four additional experiments in 1952, the results were the same. Averages for all eight experiments showed the tank-mix formulation to have exceeded Zerlate in potato yield by 15 bushels per acre, and to have held defoliation to 31 percent, whereas it was 36 percent on the plots treated with Zerlate.

Methasan and SDDC plus $ZnSO_4$ were compared on tomatoes at Wooster in 1951, and the same tank-mix formuation was used in comparison with Zerlate on tomatoes in 1952. Early blight was of only medium severity during both seasons and late blight was absent. Anthracnose did not cause any appreciable loss even in the untreated check plots. Data averages for the two years showed an average yield excess in favor of the tank-mix formulation of 2.6 (15%) tons per acre. The average degree of defoliation on the plots sprayed with Zerlate and Methasan was 57 percent, whereas it was only 44 percent on those treated with SDDC plus $ZnSO_4$. The latter also gave better control of anthracnose than the wettable powders, and slightly fewer culls.

Zac as a slurry was compared with the wettable powder in two experiments on tomatoes, one in 1950 and one in 1951. In 1950, during a late blight epidemic, the slurry gave better control of late blight on the foliage and fruit, and also of anthracnose, than did the wettable powder. These results correspond with those obtained when Methasan slurry was compared with dry Methasan. In 1951 Zac slurry gave somewhat better control of defoliation caused by early blight, and of anthracnose, than that given by the dry formulation.

Tank-mix Zac gave better control of early blight on potato in an average of four experiments in 1951 than did Zerlate. There was 40 percent of defoliation in the Zerlate-treated plots and only 30 percent on those that received SDDC-A pus $ZnSO_4$. Plots treated with the tank-mix Zac yielded 15 bushels per acre more than those sprayed with Zerlate. In 1952, Zac as a wettable powder did not control defoliation of potatoes due to early blight as well as the tank-mix formulation, and the latter gave the larger yield by 20 bushels per acre. On tomatoes in 1951, early blight was better controlled by SDDC-A plus $ZnSO_4$ than by dry Zac, the respective percentages of defoliation being 36 and 52. This carried through to influence the yields also, since the Zac-treated plots produced 17.0 tons per acre, whereas there were 19.2 tons on those that received the tank-mix formulation. The differences were even greater in 1951 when the Zac-treated plots showed 87 percent defoliation and produced a total yield of 15.2 tons per acre, whereas the defoliation was reduced to 51 percent by the tank mixture and the yield was increased to 19.1 tons.

Tank-mix formulations of ferbam (Fermate) were used on potatoes in 1952 merely to complete a series of the dimethyl dithiocarbamates, since this fungicide is seldom recommended for use on vegetables. On potatoes, the wettable powder was closely comparable to the tank-mix preparation and both were somewhat phytotoxic. On

tomatoes, SDDC plus ferric sulfate was slightly more effective than the wettable powder (Fermate) but there was little to choose between the two formulations, and both were again somewhat injurious to the foliage. Nabam plus ferric sulfate as a tank-mix formulation was closely comparable to Fermate and to SDDC plus ferric sulfate in the control of early blight on potato and tomato in 1952. All three formulations were quite injurious to tomato foliage and in addition they gave comparatively poor control of early blight.

Vancide 51, which is a mixture of SDDC and 2-mercaptobenzothiazole, was also compared in two formulations on potatoes and tomatoes in 1951 and 1952. In 1951, Vancide 51 plus $ZnSO_4$ gave better control of early-blight defoliation and produced a larger average yield in four experiments on potatoes than did Zerlate. In 1952, the same tank-mix formulation gave better control of early blight and a larger yield of potatoes than a wettable powder form of Vancide ZW. The same was true on tomatoes in 1951 and 1952 when Vancide 51 plus $ZnSO_4$ gave the better control of defoliation due to early blight, and its use resulted in a larger yield than was obtained with wettable powder formulations of Vancide.

In an average of 15 experiments performed during a 5-year period, Dithane D-14 (nabam) plus zinc sulfate gave only a 2 bushel per acre increase over Dithane Z-78 (zineb), and it gave only a one percent greater decrease in defoliation caused by early blight alone or in combination with late blight.

On tomatoes, in an average of 10 experiments covering a period of 5 years, plots treated with the tank-mix formulation of Dithane D-14 plus $ZnSO_4$ compared very closely with those that received Dithane Z-78. In comparison with the wettable powder, the plants treated with the tank-mixture produced 0.3 tons per acre fewer tomatoes, had 3.0 percent fewer culls, showed 1.1 percent more defoliation and 1.2 percent less late blight on the fruits.

Manzate as a wettable powder has been compared with a spray-tank mixture of nabam and manganese sulfate in eight experiments on potatoes, four in 1951 and four in 1952. Early blight was severe in three of these and medium to slight in the other five. Manzate gave an average excess in yield over the tank-mix formulation of 2 bushels per acre. The average degree of defoliation on the plots sprayed with Manzate was 33 percent, whereas it was 39 percent on those treated with nabam plus $MnSO_4$.

In three experiments on tomatoes (two in 1951 and one in 1952) in which early blight was present in medium severity and late blight was

absent, Manzate gave an average net yield of 13.8 tons per acre compared with 13.5 tons for the tank-mix formulation. Defoliation was better controlled by Manzate, with 36 percent present, whereas the tank-mix plots showed 51 percent. Four percent of the tomatoes produced on plots treated with nabam plus $MnSO_4$ were culls, whereas there were 3.5 percent of culls on those that received Manzate.

$MnSO_4$ was also added to SDDC and used on potatoes and tomatoes at Wooster in 1952. This manganese dimethyl dithiocarbamate gave as good results in the experiment on potatoes as did nabam plus $MnSO_4$, but neither gave as good control of early blight as did Manzate. On tomatoes, this tank-mix formulation of SDDC and $MnSO_4$ was definitely inferior to Manzate in all categories of disease control, and somewhat inferior to nabam plus $MnSO_4$.

CONCLUSIONS

This summary of the performance of various formulations of the dithiocarbamates in the control of early and late blights on potatoes and tomatoes grown in Ohio suggests the following conclusions:—

1. That ziram used as a slurry, which is not dried following its manufacture, is more effective as a fungicide than when the spray mixture is formulated from a wettable powder.
2. That ziram used as a tank-mix formulation, prepared by adding water-solubilized $ZnSO_4$ to a partially diluted solution of sodium dimethyl dithiocarbamate (SDDC) will give considerably better control of these foliage diseases than will ziram used as a wettable powder.
3. That the tank-mix equivalent of Zac prepared by adding $ZnSO_4$ to SDDC-A (a sodium dimethyl dithiocarbamate-cyclohexylamine complex) will give much better control of these diseases than will Zac formulated from the wettable powder.
4. Likewise, the tank-mix product obtained by adding solubilized $ZnSO_4$ to Vancide 51 is more efficient in the control of these tomato and potato diseases than any of the wettable powder formulations so far submitted by the manufacturer.
5. Dithane and Parzate prepared as wettabe powders (zineb) are very closely comparable in their disease-control efficiency with their respective tank-mix formulations obtained by adding nabam to a solution of $ZnSO_4$ in water.
6. Manganese ethylene bis dithiocarbamate prepared as a tank-mix formulation by adding nabam to solubilized $MnSO_4$ has been somewhat more erratic and unpredictable in its fungitoxic action than

has the corresponding wettable powder (known under the trade of Manzate).

Finally, the excellent performance record of tank-mix formulations of ziram, prepared by adding SDDC (and certain complexes that contain it) to a solution of $ZnSO_4$ in water, in the control of early blight on potato, and early blight and anthracnose of tomato, suggests that this mixture should be thoroughly tested on the experimental level for the control of not only these diseases but all foliage diseases of these and other vegetables. The degree of control of late blight obtained with the slurry form of ziram indicates that the tank-mix formulations also may be expected to give much better control of that disease than was ever obtained with the wettable powder formulations of this fungicide. Thus, the Ohio grower of early potatoes, which are very seldom attacked by late blight, might well try this tank-mix formulation of ziram in comparison with Zerlate, Manzate, Dithane, or Parzate. The tank-mix formulation of manganese ethylene bis dithiocarbamate ($MnSO_4$ plus water plus nabam) might also be tested in the same way, but extreme care must be used in its preparation if a dependable fungicide is to be obtained, and even then the result, in terms of disease control, is somewhat unpredictable.

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APPENDIX

Directions for the preparation of tank-mix formulations of the dithiocarbamate fungicides

These fungicides are of several kinds. The list of chemical ingredients used in their preparation includes disodium ethylene bis dithiocarbamate (nabam), sodium dimethyl dithiocarbamate (SDDC), a complex of SDDC and cyclohexylamine (SDDC-A), and a 50-50 mixture of the sodium salts of dithiocarbamic acid and 2-mercaptobenzothiazole (Vancide 51), all of which are amber-colored liquids. At least three metal sulfates may be added to one or another of these liquids to make the tank-mix formulation desired. For instance, SDDC plus

$Fe_2(SO_4)_3$ gives a tank-mix formulation of ferbam, SDDC plus $ZnSO_4$ results in the formation of ziram, SDDC-A plus $ZnSO_4$ gives the tank-mix equivalent of Zac, and Vancide 51 plus $ZnSO_4$ gives the zinc salt of that complex. If $ZnSO_4$ is added to nabam, the reaction product is zineb, and the use of $MnSO_4$ with nabam results in a tank-mix formulation of manganese ethylene bis dithiocarbamate.

All of these tank-mix formulations, with the possible exception of the one in which nabam is added to $MnSO_4$, are comparatively easy to prepare. For experimental purposes the metal sulfate to be used (iron, zinc, or manganese) was first solubilized in 10 to 20 times its weight of water in a white, enamelled 3-gallon pail. Then, the selected dithiocarbamate liquid (nabam, SDDC, or a modification of the latter) was added to the solubilized sulfate with rapid stirring. This mixture was then added to the spray tank, which already contained about half of the water to be used, and enough water was added to give the desired volume of spray mixture. Constant agitation is desirable. Most of the experimental mixtures used during the past two seasons were prepared with pre-solubilized solutions of ferric, zinc, or manganese sulfate, the required amount of which was measured out just as was the liquid sodium salt of whatever dithiocarbamate was to be used. In these instances, the solubilized sulfate was first diluted with several times its volume of water and the second liquid added during good agitation.

The same general plan can be used in making manganese ethylene bis dithiocarbamate except that the recommended procedure must be adhered to very closely, and even then there seems to be a much greater variation in the character of the resulting precipitate than is the case with $ZnSO_4$. For the production of only a few gallons (10 to 20), the necessary amount of $MnSO_4$ is dissolved in at least one quart of water. Then add the required amount of nabam to the $MnSO_4$ solution and stir until a creamy precipitate is formed, usually in about one minute. This slurry may then be added to the sprayer tank and diluted with the required amount of water. The user can prepare larger amounts of any of these tank-mix formulations by using equipment of appropriate size.